Electrochemically Stable High Energy Density Lithium-Sulfur Batteries

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Project ID #bat446

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Overview

Timeline

- Project start date:
  - April 1, 2019
- Project end date:
  - March 31, 2021
- Percent complete: 50%

Budget

- Total project funding
  - DOE share: $800, 000
  - Cost share: $88, 928
- Funding received in FY 2019: $439, 129
- Funding for FY 2020: $449, 799

Barriers

- Barriers addressed
  - Limited Cycle life
    - (polysulfide dissolution)
  - Low coulombic efficiency
  - Poor rate capability
    - (poor electronic and Li ion conductivity)

Partners

- Interactions/collaborations
  - UPitt (D. K. Achary)
  - Malvern Panalytical (S. Speakman)
  - Kurt J. Lesker Co. (KJL)
  - Flex Cellz

Relevance/Objectives

Objectives:

Research, develop, and demonstrate a single layer/multilayer lithium sulfur battery (LSBs) pouch cell using optimized electrodes to achieve the areal capacity (≥4 mAh/cm^2), CE (≥99.9%), and cycle life (~1000 cycles with fade in capacity ≤0.001% per cycle), capable of achieving a cell energy density ≥500 Wh/kg and a life of ≥1,000 cycles.

Proposed solution:

- Development of high throughput, high yield commercially inexpensive process for the synthesis of electrochemically stable S based cathode materials/architectures
- Fabrication of high loading (≥6 mg/cm^2) sulfur-rich electrodes (≥64 wt% sulfur in the electrode) exhibiting ≥1000 mAh/g (active material basis) capacity with excellent life-cycle (>1000 cycles) and high >99.9% CE when tested with dendrite-free lithium metal anode (LMAs)
- Improve and optimize the materials performance (≥1000mAh/g, CE≥99.9) and cycle life (~1000 cycles) of selected cathode material
- Fabrication, performance testing and optimization of ~20cm^2 pouch cell of targeted energy density (≥500 Wh/kg) meeting the DOE-battery500 goals

Impact:

- Development of framework materials enabling chemical binding of polysulfides (PSs) and catalytic promoters for PS conversion using economic precursors (~$23/kg) will fulfil the target of production cost of LSB (≤$100/kWh) with a projected lithium cost of ~$100/kg and initial cost of producing of 10Ah pouch cell rated at 2V being ~USD 800-900 at NECST laboratory.
- Success of the proposed work will thus result in demonstrating LSB technology as a viable energy storage system for EV.

Milestones for 2019 and 2020

Date	Description	Type	status
April 2019	Synthesis Directly Derived Sulfur Architecture-Polysulfide Trapping Agent (DDSA-PTA) electrode to meet the targeted capacity and cycle life (~1000 cycles)	Technical	completed
April 2019	Synthesis of IFM-S and CFM-S, and CLiP-SCP-LIC coated electrodes exhibiting targeted capacity ~1000mAh/g and cycle life ~1000 cycles (≤30% fade in capacity)	Technical	completed
July 2019	Synthesis, characterization and performance study of functional catalyst based highly porous IFM and carbon-based CFM	Technical	completed
Nov 2019	Verification of achievable areal capacity ≥6mAh/cm^2, and cycle life ~1000 cycles; <0.01% fade/cycle	Go/No-Go	completed
April 2020	Large area electrodes meeting the targeted capacity: ≥6mAh/cm^2, and cycle life ~1000 cycles; <0.01% fade/cycle	Technical	ongoing
Aug 2020	Pouch cell with optimized 3-D electrodes and LMA anodes: areal capacity ≥6mAh/cm^2, cycle life (>1000 cycles), and 10% capacity fade	Technical	ongoing
March 2021	Final full cells of specific energy >500 Wh/kg, cyclability (>1000 cycles), meeting MIL-STD-810G and IEC62133 Industry safety standards. 12 cells will be delivered to DOE.	Technical	ongoing

*Acronyms are explained in the next slide

Approach

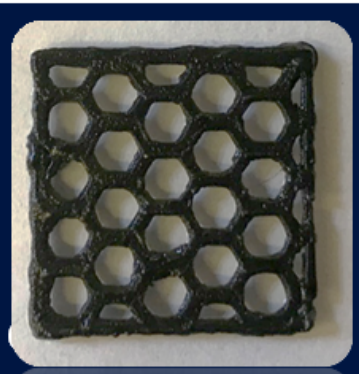
Several approaches outlined below were developed and studied:

- **Generation of novel high loading directly derived sulfur architecture (DDSA) binder free cathodes and unique polysulfide trapping agent (PTA) configurations exhibiting targeted capacity (≥1000 mAh/g) and cycle life (~1000 cycles)**
- **Generation of novel composite framework materials (CFM) enabling high sulfur loading and polysulfide (PS) confinement**
- **Interface engineering of CFM-S by homogeneous non-porous high electronic conducting (EC) and Li-ion conducting (LIC), conjugated Li-polymer sulfur containing polymer (CLi-P-SCP) PS dissolution resistant coatings to confine PSs, and improve the cycle life and rate capability.**
- **Identification of functional catalysts (FCs) for rapid conversion of PS to Li_2S and Li_2S to Li and S. Incorporation of FC during S infiltration to promote PS conversion kinetics to Li_2S and as a result, improve the cycle life.**
- **Development of novel 3D architecture electrode using EC and LIC coated CFM-S of targeted capacity (≥6mAh/cm^2) using 3D printing to achieve the desired architecture (control porosity, and thickness) guided by computational analysis.**
- **Development of single layer (~20cm^2) pouch cell targeting Batt 500 goals (energy density ≥500Wh/kg, cycle life ~1000 cycles), and deliver final full cell meeting the performance and safety standard**

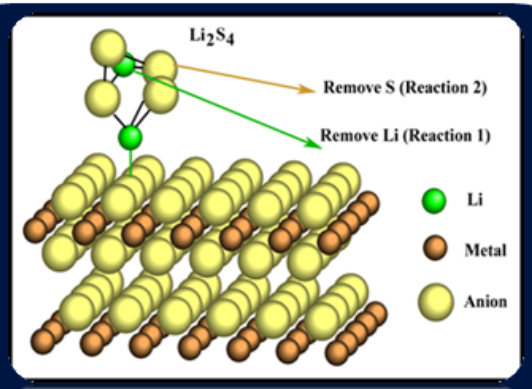
Any proposed future work is subject to change based on funding levels

Approach

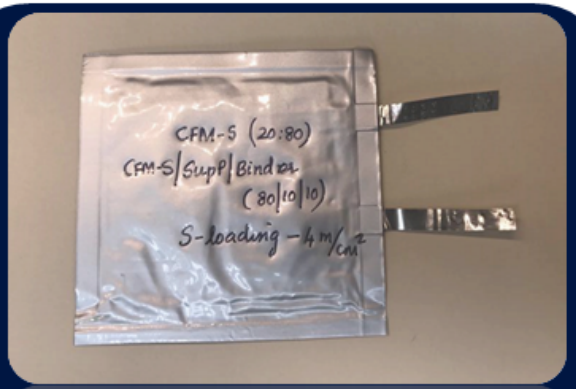
Composite framework materials based systems Studied



- EC-CFM-S
- LIC-CFM-S
- 3D printed LIC-CFM-S



FC-CFM-S



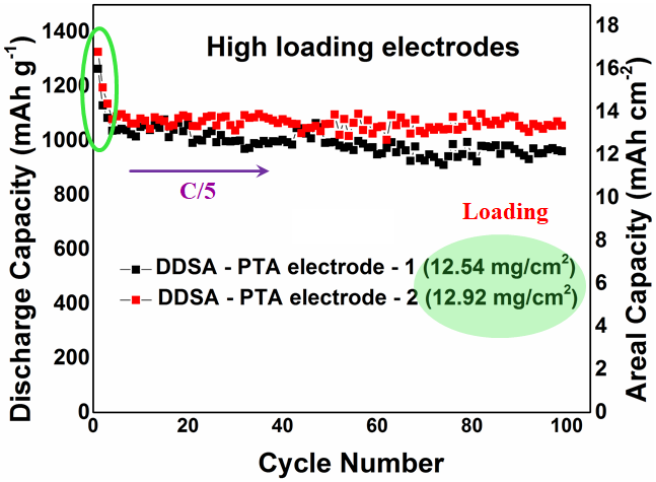
Pouch cell testing

CFM – Complex framework material
EC – Electronic conductor
LIC – Lithium ion conductor
FC – Functional catalyst

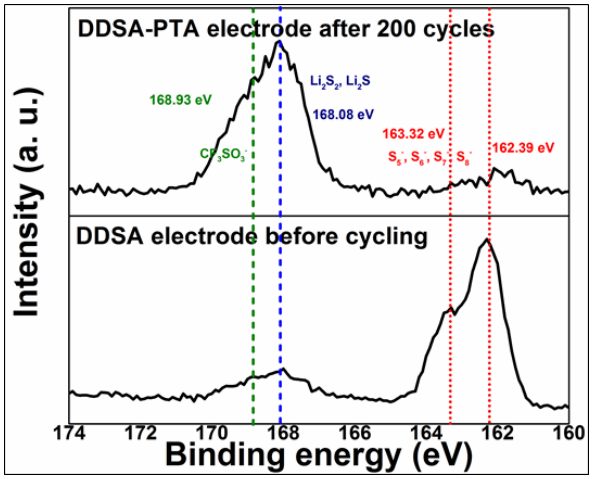
Technical Accomplishments and Progress

Directly Deposited Sulfur Architecture with PTA (DDSA-PTA)

Tested with lean electrolyte (3µl/mg) using Battery500 testing protocol



Post Cycling XPS of electrode



- **The S_{2p} spectrum of DDSA electrode after 200 charge-discharge cycles shows peaks corresponding to the higher order and lower order polysulfide (~162 eV and 163 eV)**
- **The DDSA – PTA electrode peaks corresponding to lower order polysulfides (Li_2S_2 and Li_2S) probably due to the binding and subsequent reduction of polysulfides to disulfides**
- **The S_{2p} spectra of both DDSA and DDSA-PTA electrode showed peak corresponding to $CF_3SO_3^-$ group from the Li salt from the electrolyte**
- **The PTA effectively binds and traps the polysulfides**

Coin cell testing protocol and results	
Formation process and charge/discharge rate	2 cycles at C/20 rate Subsequent cycling: C/5
Electrolyte : 1M LiTFSI- DOL/DME (1:1) + 2wt.% LiNO3	Electrolyte to capacity ratio= 3g/Ah (3 µl/mg S active material)
Voltage	1.8V-2.6V
Areal capacity	8-10 mA/cm2

Limitation: The substrate used for DDSA-PTA has poor electronic conductivity leading to poor rate capability

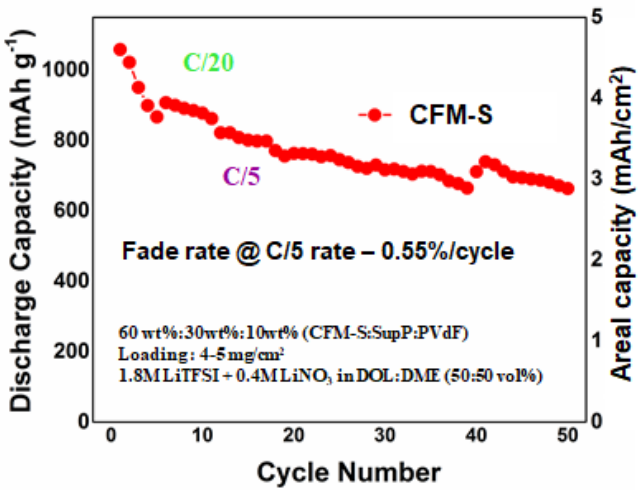
Future work: Electrophilic metal such as Ti and Al foam or mesh will be used as PTAs to improve the rate capability will be tested in the pouch cell configuration

Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

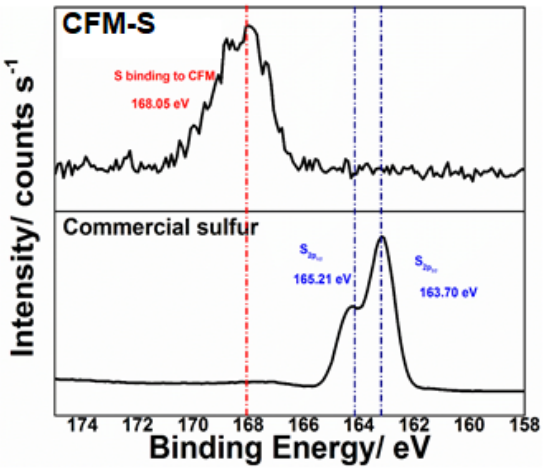
Complex Framework Material (CFM-S)

Tested with lean electrolyte (4µl/mg) using Battery500 testing protocol

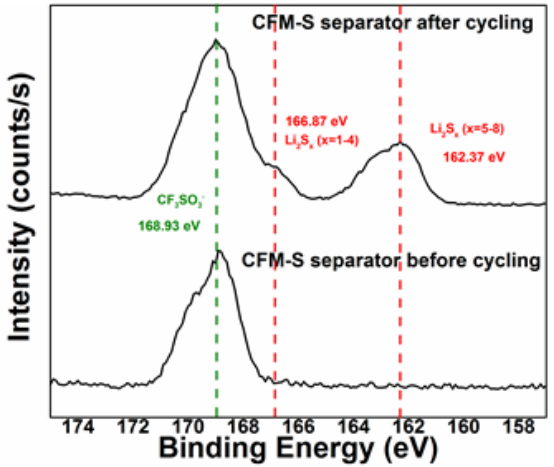


Poor cycle life

Post Cycling XPS of electrode



Post Cycling XPS of separator



XPS analysis of the CFM separator shows low and higher order polysulfides

Limitation:

The CFM has low surface area (3.64 m^2/g) and pore volume (0.008 cm^3/g)

The CFM has poor electrical ($\sigma = 4.13 \times 10^{-7}$ S/cm*) and ionic ($\sigma = 2.47 \times 10^{-5}$ S/cm*) conductivity

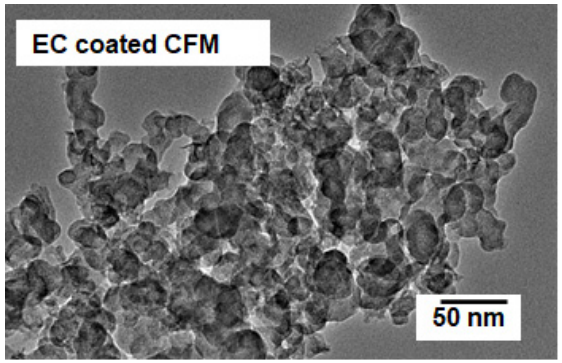
Needs to improve the electrical conductivity and Li ion conductivity of CFM based materials

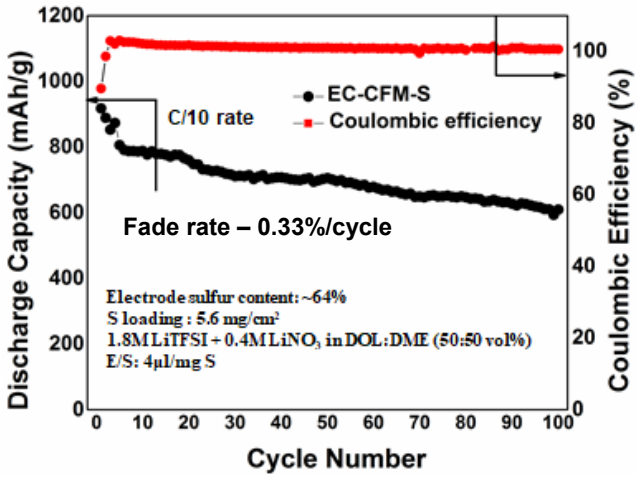
- **Interfacial engineering of CFM-S using EC and LIC**

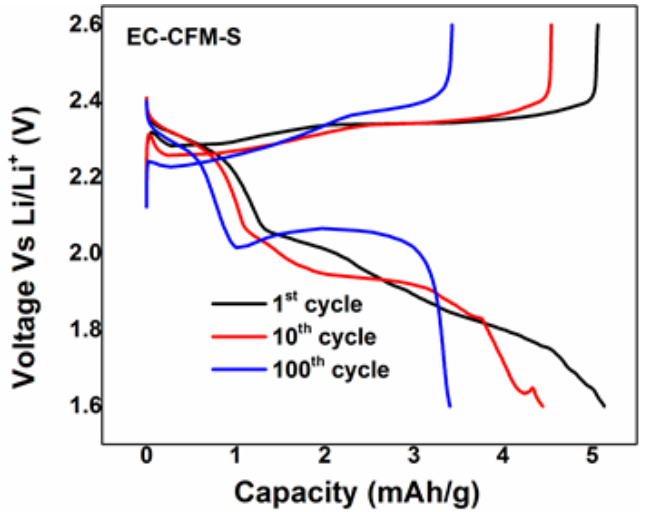
Any proposed future work is subject to change based on funding levels

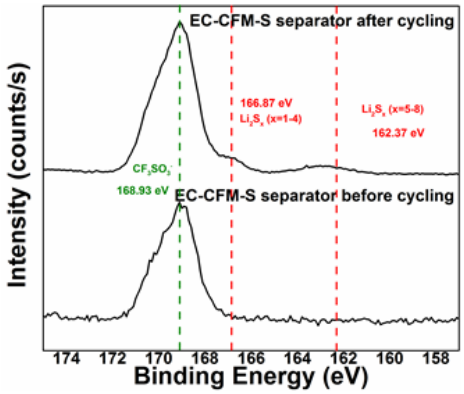
Technical Accomplishments and Progress

Interface Engineering: Electronic conductor coated CFM (EC-CFM-S)









XPS analysis before and after cycling

- Capacity fade rate: 0.33 % per cycle
- The EC-CFM has high surface area (227 m^2/g) and pore volume (0.6 cm^3/g)
- Coating of CFM with EC improves electronic conductivity (~10^{-4} S/cm)
- Reduced polysulfide dissolution (XPS) and high areal capacity (>3mAh/cm^2)

EC coated CFM of nanocrystalline porous architecture shows ability to trap PS improving the areal capacity

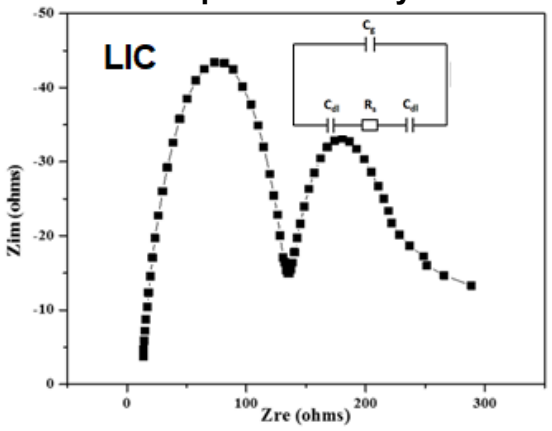
Future work: will be tested in the pouch cell configuration to achieve the targeted energy density

Any proposed future work is subject to change based on funding levels

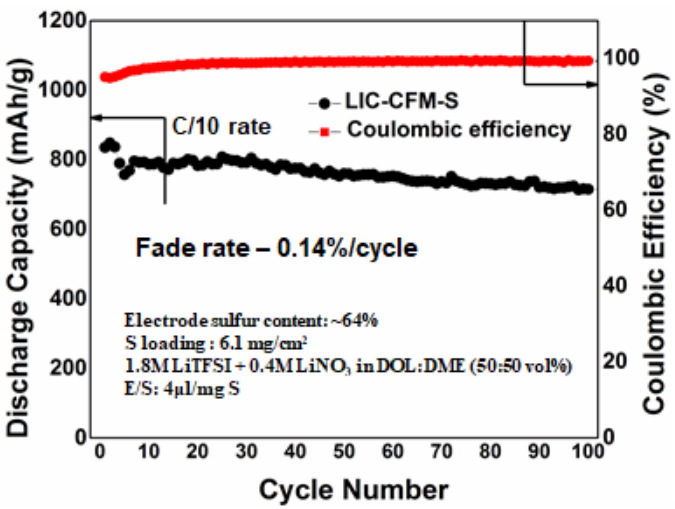
Technical Accomplishments and Progress

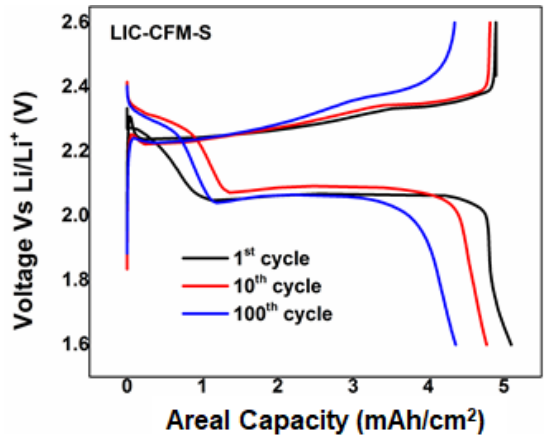
Interface Engineering: Li-ion conductor coated S infiltrated CFM (LIC-CFM-S)

Impedance analysis



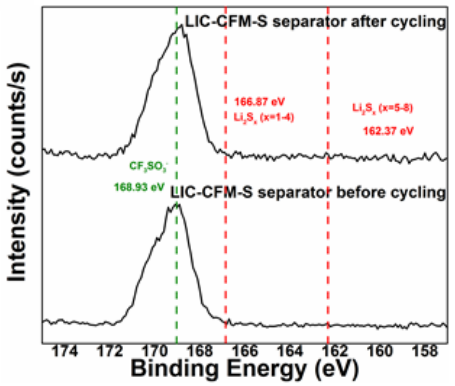
$\sigma = 3.25 \times 10^{-4}$ S/cm





- Coating CFM with LIC improves ionic conductivity (3.25 * 10^{-4} S/cm)
- The LIC-CFM has high surface area (209 m^2/g) and pore volume (0.62 cm^3/g)
- The LIC-CFM-S exhibits high areal capacity of 4.3 mAh/cm^2 after 100 cycles with fade in capacity ~0.14 % per cycle
- Significant improvement of stability and cyclability

LIC coated CFM of nanocrystalline porous architecture shows excellent ability of trapping PS improving the areal capacity

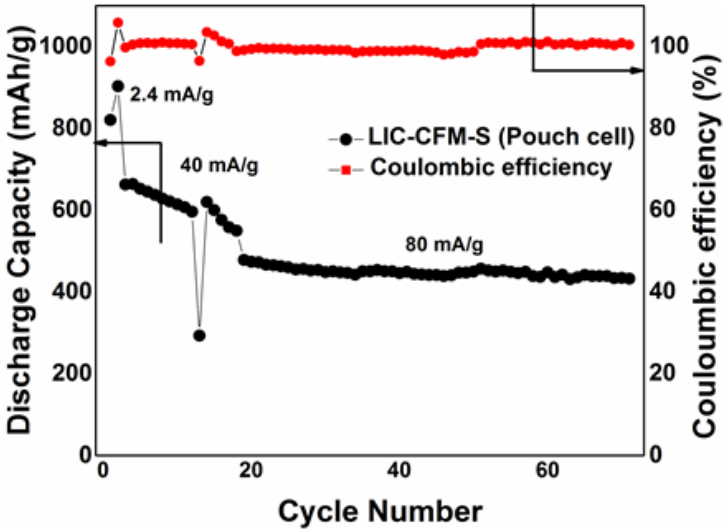


XPS analysis
: No PS dissolution

Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

Pouch cell feasibility test of LIC-CFM-S



S loading: 2.4 mg S/cm^2
E/S ratio: 10ul/mg S
Electrolyte: 1.8M LiTFSI + 0.4M $LiNO_3$ in 50:50vol% DOL:DME
Electrode composition: LIC-CFM-S/SuP/PVdF (60/30/10)
LIC-CFM-S composition: LIC-CFM/S (20/80)
Electrode sulfur content: 48% S

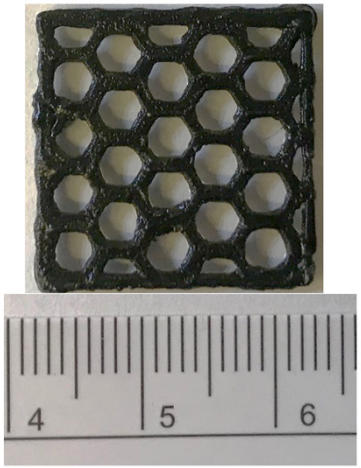
Single layer pouch cell – feasibility test

- Single layer sulfur cathode yielded 42 mWh energy density
- Efforts to optimize E/S ratio and pouch cell pressure during cycling are underway
- Cycling stability studies and optimization are currently ongoing

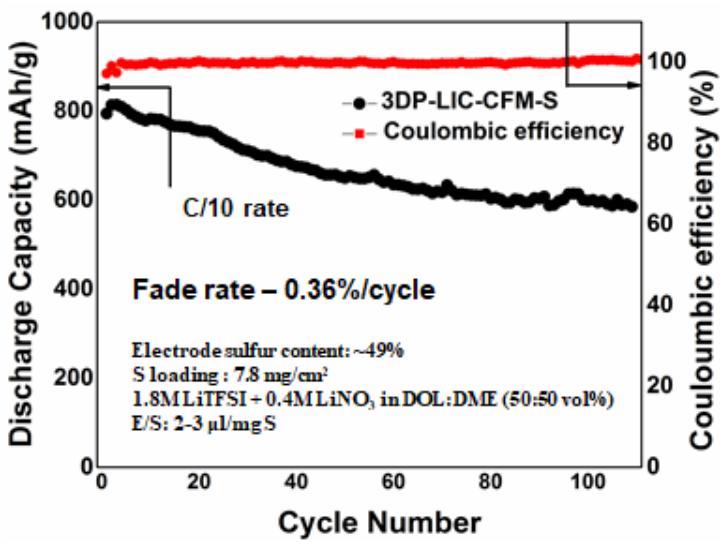
Any proposed future work is subject to change based on funding levels

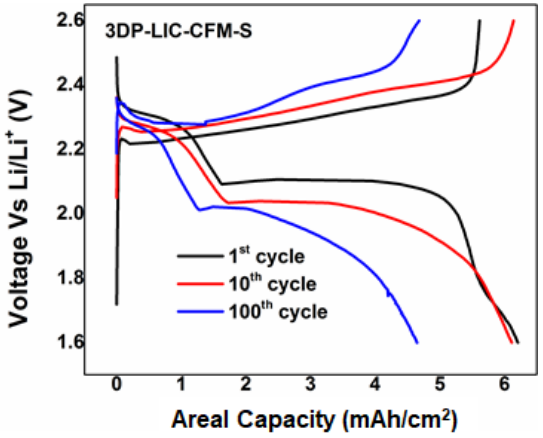
Technical Accomplishments and Progress

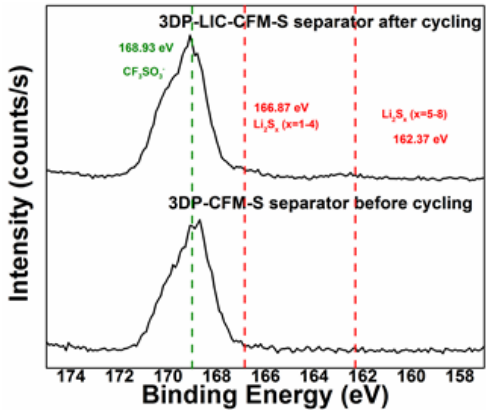
3D printed cathodes of LIC-CFM-S for Li-S batteries (Tested with Composite Polymer Electrolyte (CPE)



3D printed cathode







XPS analysis

- The 3DP-LIC-CFM-S exhibits high areal capacity of 4.8 mAh/cm² after 100 cycles
- The 3DP-LIC-CFM-S separator shows no polysulfide dissolution after cycling

3DP –LIC-CFM-S of nanocrystalline porous architecture shows ability to trap PS improving the areal capacity

Future work: Fabrication and characterization of ~20 cm² single layer pouch cell using the optimized 3D electrode architecture.

Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

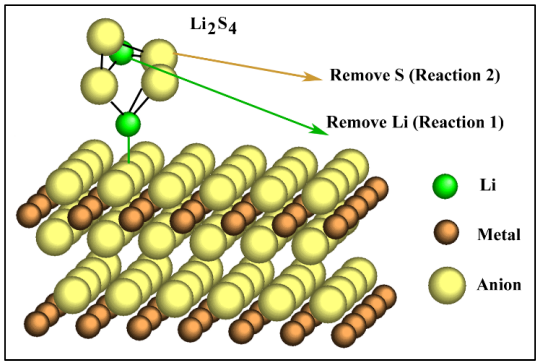
Computational Identification of Functional Catalysts for rapid conversion of PSs to Li_2S and elemental Li+S

- **Accelerate the PSs conversion reaction in the forward direction to form Li_2S and backward direction to form pure Li and S**
- **There is a need to identify a suitable catalyst material for facilitating the following two forward and backward reactions:**

$$2Li^+ + 2e^- + (m/8)\,S_8 \overset{(1)}{\leftrightarrow} Li_2S_m \overset{(2)}{\leftrightarrow} Li_2S + [(m\text{-}1)/8]\,S_8\,, \qquad m = 1,2,3,\ldots,8$$

- **Facilitating these reactions will help significantly decrease or even completely eliminate the PSs dissolution**

Reaction 122	Reaction 2
Li2S8 -> LiS8 + Li*	Li2S8 -> Li2S6 + 2S*
Li2S6 -> LiS6 + Li*	Li2S6 -> Li2S4 + 2S*
Li2S4 -> LiS4 + Li*	Li2S4 -> Li2S2 + 2S*
Li2S2 -> LiS2 + Li*	Li2S2 -> Li2S + S*



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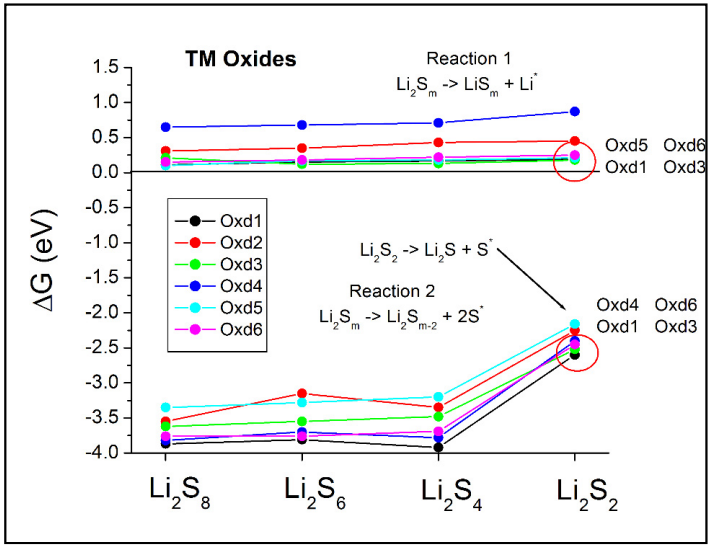
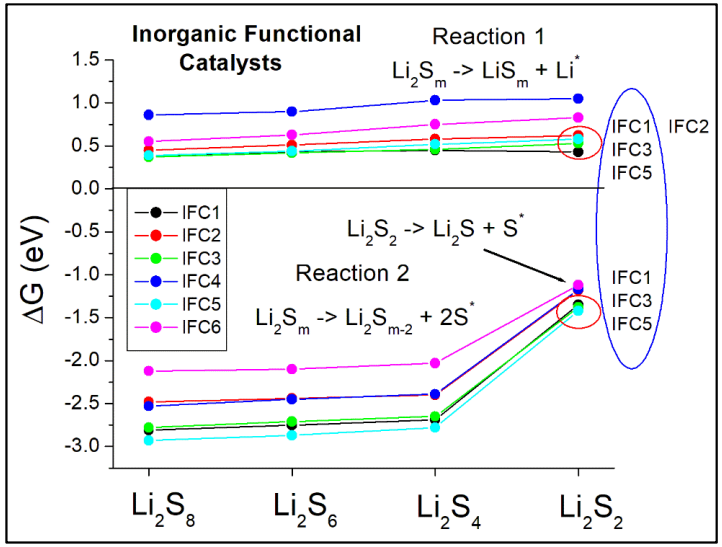
Technical Accomplishments and Progress

Ab-initio calculations of the PSs decomposition free energies





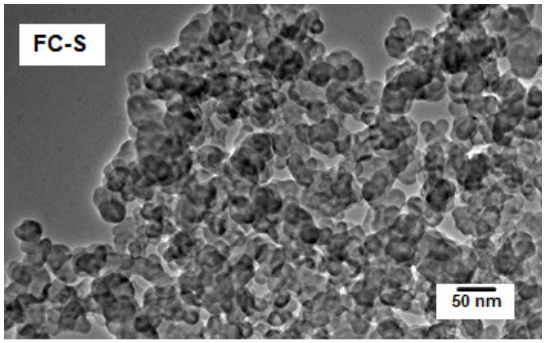
- **The decomposition energies ΔG of the various PSs are different for different catalytic materials. The best catalysts could be characterized by the lowest free energy for both Reaction 1 and Reaction 2 directions.**

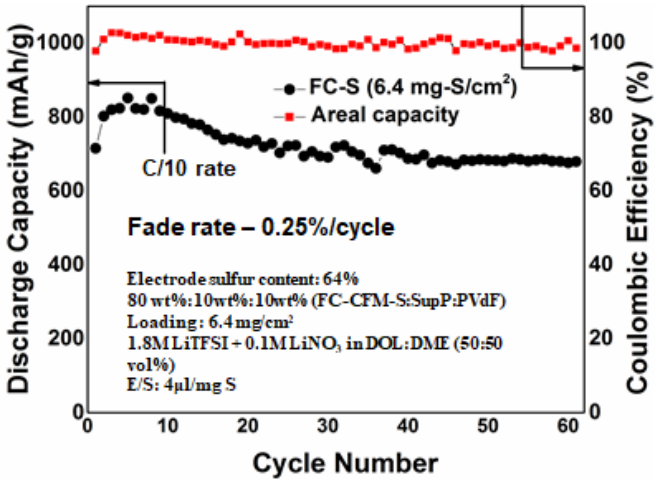
The experimental validation of these theoretical findings are on-going
Future work: other potential functional catalytic materials will be considered using this computational approach

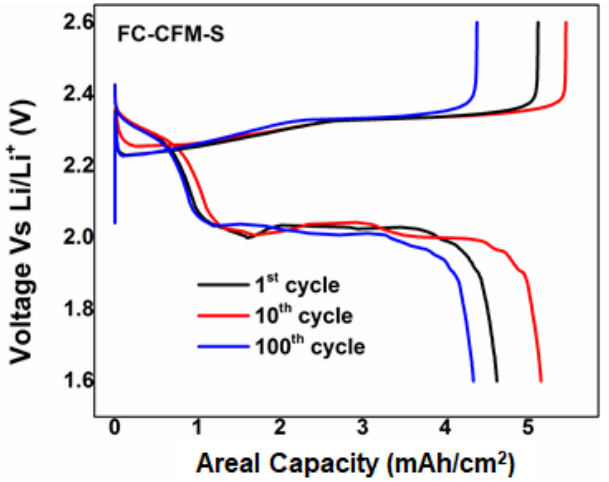
Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

Sulfur infiltrated Functional Catalyst (FC-CFM-S) System

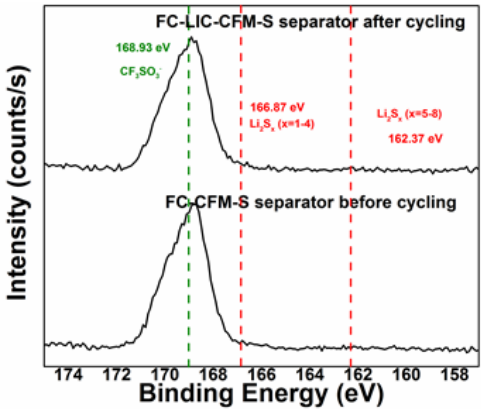






- The FC-CFM has high surface area (162 m^2/g) and pore volume (0.63 cm^3/g)
- FC prevents polysulfide dissolution into electrolyte (XPS)
- The FC-CFM-S exhibits high areal capacity of 4.3 mAh/cm^2 after 60 cycles
- Excellent cycle life and no PS dissolution

FC-CFM-S of nanocrystalline porous architecture shows ability to trap PS improving the areal capacity



Any proposed future work is subject to change based on funding levels

Responses to Previous Year Reviewers' Comments

- The project was not reviewed last year.

Collaboration and Coordination with Other Institutions

Dr. D. Krishnan Achary (University of Pittsburgh): Solid-state nuclear magnetic resonance (MAS-NMR) characterization to study the failure mechanisms

Malvern Panalytical: Materials and phase evolution characterization using in-situ XRD

Kurt J. Lesker Company (KJL): Thin film deposition and vacuum instrumentation

Flex Cellz: Technology Licensing Partner

Nanomaterials for Energy Conversion Storage Technology (NECST) Laboratory–Energy Innovation Center, Pittsburgh: Development of modified coin cell testing and carbon nanoarchitectures, development of pouch cell testing

Any proposed future work is subject to change based on funding levels

Remaining Challenges and Barriers

- **Challenges**
  - **Interface engineering**: Scale up of coating technology with EC and LIC materials on the surface of LSBs electrode to ensure good interface adhesion, PS confinement as well as interface strength of LIC to electrode and LIC-electrolyte interface.
  - Overcome low coulombic efficiency by controlling the SEI layer formation in surface engineered and scaled up electrodes.
  - Fabrication and characterization of ~20 cm^2 single layer pouch cell using the optimized 3D electrode architecture.
  - **Fabrication of single layer/multilayer (~20cm^2) pouch cell targeting Batt 500 goals (energy density ≥500Wh/kg, cycle life ~1000 cycles)**
- **Barriers**
  - Possible barriers include accounting for scale up related variability in achieving reproducible performance due to increasing thickness of electrodes.
  - Matching performance of pouch cell configuration with coin cell results

Future Work

- **Fabrication, battery performance characterization and scale up of high S loading (≥6mg/cm^2) LIC-CFM-S electrode of targeted capacity (≥6mAh/cm^2)**
  - Fabrication of large area optimized electrode architecture (≥100 cm^2) of desired thickness and porosity using suitable electrode fabrication parameters (e.g. calendaring), slurry composition, viscosity, and particle morphology. The large area high sulfur loading electrode is to be used in the pouch cell fabrication.
- **Fabrication of single layer pouch cell (~20cm^2, targeted capacity: ~100 mAh cell) with optimized S electrodes, nano-filler containing CPE as separator and in-house synthesized Li metal alloy anodes (~100μm) to achieve the Batt 500 targeted goals in pouch cell configuration.**
  - Formation cycle and cell balancing of the optimized system.
  - Constant current-constant voltage (CCCV) test protocol to determine nominal discharge capacity at 100% state of charge (SOC).
  - Constant current-constant voltage (CCCV) test protocol to determine nominal discharge capacity at 100% state of charge (SOC).
- **Fabrication and characterization of ~20 cm^2 single layer pouch cell using the optimized 3D electrode architecture.**
- **Safety field test will be performed on ~100mAh single layer pouch cell (≥500Wh/kg) using MIL-STD-810G and IEC62133 safety standards in collaboration with PNNL and industry partner. 12 test cells meeting the performance and safety standard will be delivered to DOE.**

Summary

- **The DDSA-PTA system shows ~1000 mAh/g capacity for over 100 cycles (~12 mg/cm^2) when tested under Batt500 lean electrolyte conditions (3µl/mg)**
- **The LIC-CFM-S system shows ~4.3 mAh/cm^2 capacity for over 100 cycles (~6 mg/cm^2) when tested under Batt500 lean electrolyte conditions (4 µl/mg)**
- **The 3D printed LIC-CFM electrodes with a loading of ~8 mg/cm^2, when tested with CPE (~2-3 µm) shows high areal capacities of ~3.8 mAh/cm^2**
- **The FC-CFM-S systems, when tested at ~6.4 mg/cm^2 loadings, showed areal capacities of ~4.3 mAh/cm^2 when cycled at C/10 rate under Batt500 lean electrolyte conditions (4 µl/mg)**
- **Initial pouch cell testing of the LIC-CFM-S system show promising specific capacities (~450 mAh/g) at ~2.4 mg/cm^2 loadings and under E/S ratio (10µl/mg)**
- **DDSA and all CFM systems demonstrate promise for confining polysulfide species with high S loadings (~6 mg/cm^2) and areal capacity ~4 mAh/cm^2 under lean electrolyte conditions**

Any proposed future work is subject to change based on funding levels

Technical Back-Up Slides

Battery500 Testing Protocol for Li-S cells

Coin Cell Testing Protocol for Li/S (for FY20 350 Wh/kg milestone)	
Minimum areal capacity	**4.6 mAh/cm² (~6mg/cm² loading)**
Coin cell assembly	**CR2032 coin cell kits** **Sulfur cathode disk, 1 piece** **PE separator, 20 mm thick, ¾" diameter, 1 piece**
Baseline electrolyte: 1M LiTFSI-DOL/DME(1:1) +2% $LiNO_3$	**1. Electrolyte amount: Excessive amount of electrolyte for initial evaluation of sulfur cathode** **2. Final testing: Lean electrolyte with electrolyte/capacity ratio = 3 g/Ah**
Li metal foil: 1.56 cm diameter (1 piece)	**1. Initial testing: 250 µm Li metal foil** **2. Final testing: 50 µm Li (N/P = 2.2)**
Testing protocols	**1. Testing temperature: 25 °C** **2. Voltage range: 1.8 -2.6 V** **3. Resting time: 8 h** **4. Formation process: 2 cycles at C/20 rate** **5. Subsequent cycling:** **• Discharge at C/3 rate and charge at C/5 rate for 50 cycles. Discontinue testing when cell specific capacity falls below 70%** **• Discharge at C/1 rate and charge at C/3 rate for 100 cycles. Discontinue testing when cell specific capacity falls below 70%**

Technical Back-Up Slides

Fabrication of DDSA-PTA electrode

Synthesis of carbon fiber mat (substrate)

Step 1: 1g Polymer+ 10 ml NMP
Step 2: Electrospinning conditions
- 25 kV voltage
- 1 ml/h flowrate
- 15 cm separation

Step 3: The electrospun mats were heated at 180 C for 4 h in air followed by carbonization at 700 C for 1 h in Argon

Electrodeposition of sulfur onto the substrate

Working electrode: Carbonized polymer fiber mats
Counter electrode: Platinum
Electrolyte:
1. 24 g sulfuric acid (98%)
2. 1.5 g KOH
3. 1.0 M thiourea
4. 500 ml deionized water

Electrodeposition conditions:
Voltage: 3 – 4 V
Time: 12-24 h

Electrodeposition of polysulfide trapping agents (PTA)

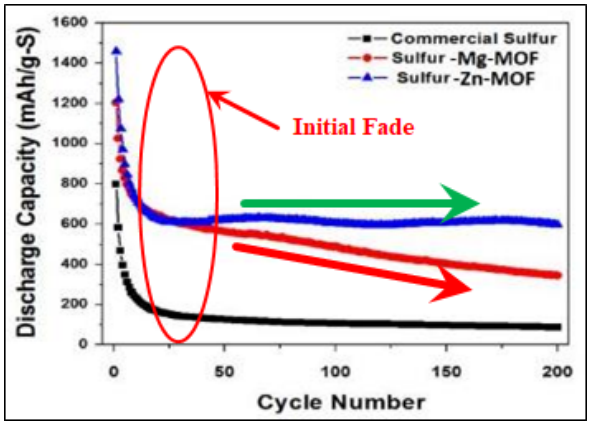
Working electrode: Sulfur containing polymer fiber mats
Counter electrode: Platinum
Electrolyte:
1. 1 M Salt solution
2. 100 ml deionized water

Electrodeposition conditions:
Voltage: -2 V
Time: 15 – 30 min

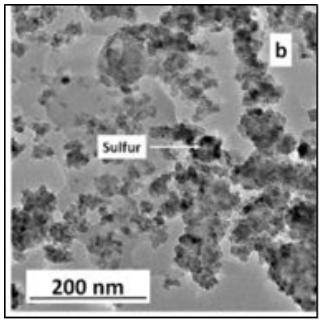
Technical Back-Up Slides

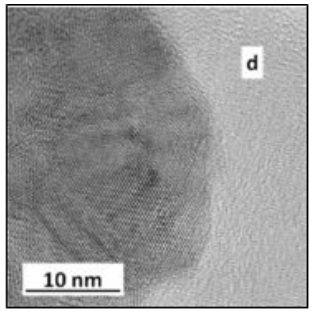
Various Complex Framework Material-Sulfur (CFM-S) (Tested with flooded electrolyte (20µl/mg))

Sulfur – Carbonate MOF (Gen I)

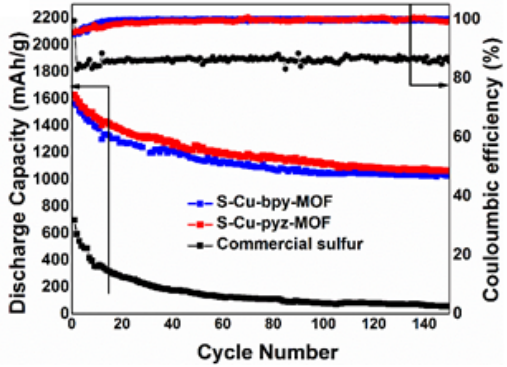


S Loading : 1.5-2 mg/cm² Cycled at 0.2C rate, 70wt% S/30wt% CFM
Electrolyte: 1.8M LiTFSI + 0.1M $LiNO_3$ in DOL:DME (50:50 vol%)

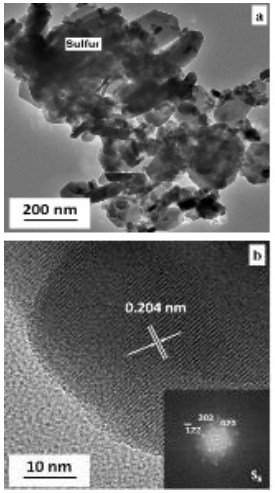




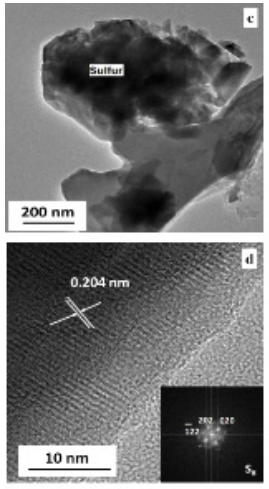
Sulfur – Pyrazine/Bipyridine MOF (Gen II)



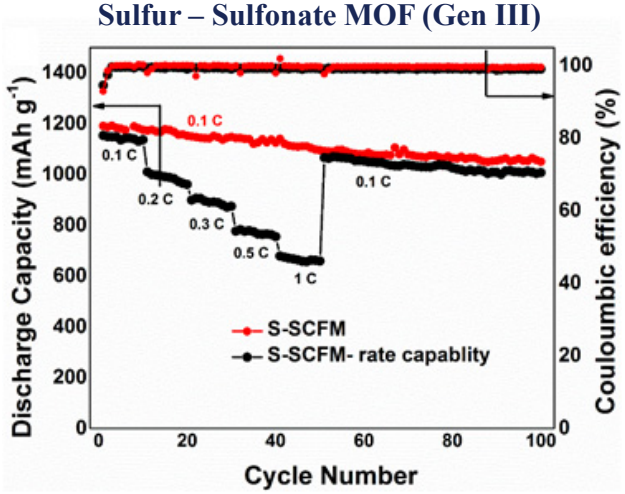
Sulfur – Pyrazine MOF



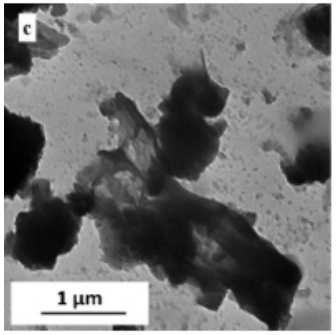
Sulfur – Bipyridine MOF



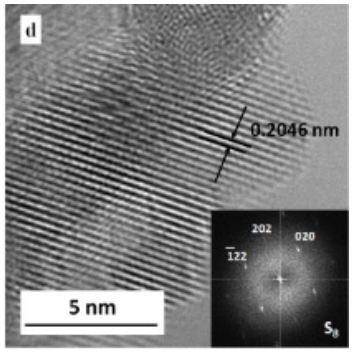
Sulfur – Sulfonate MOF (Gen III)



TEM



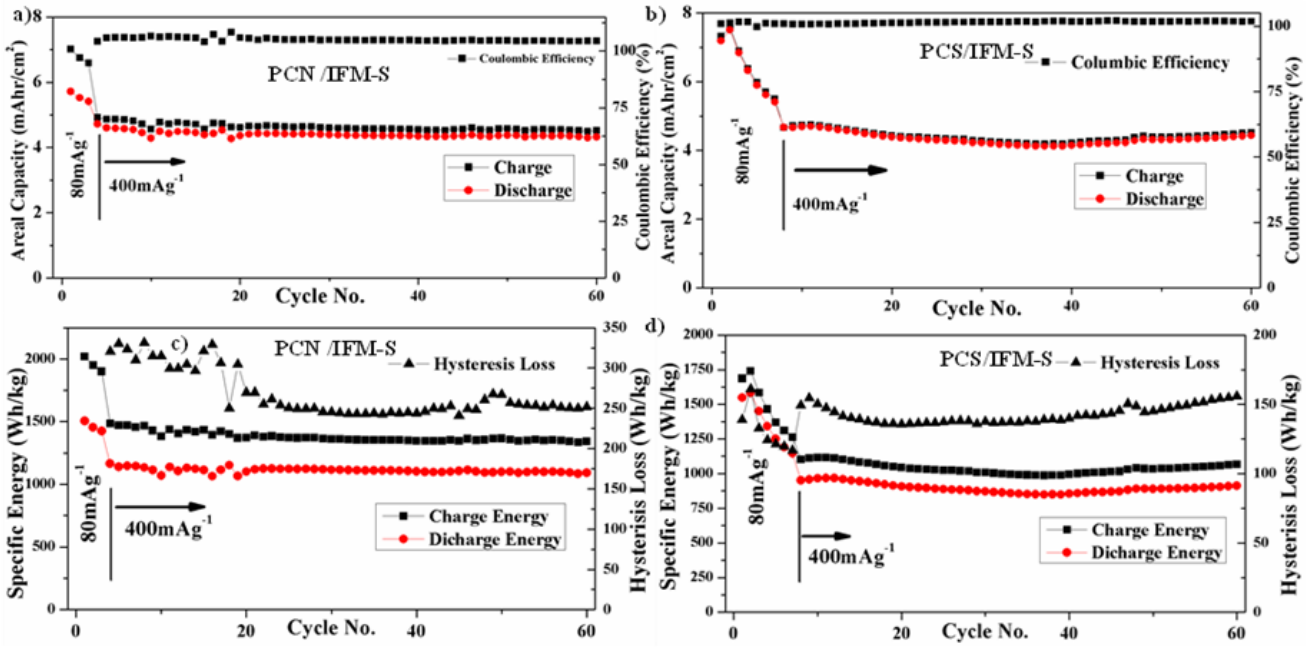
HRTEM



Technical Back-Up Slides

Inorganic Framework Material-S (IFM-S)

(Tested with extremely lean electrolyte (2µl/mg-8 µl/mg) using Battery500 testing protocol)

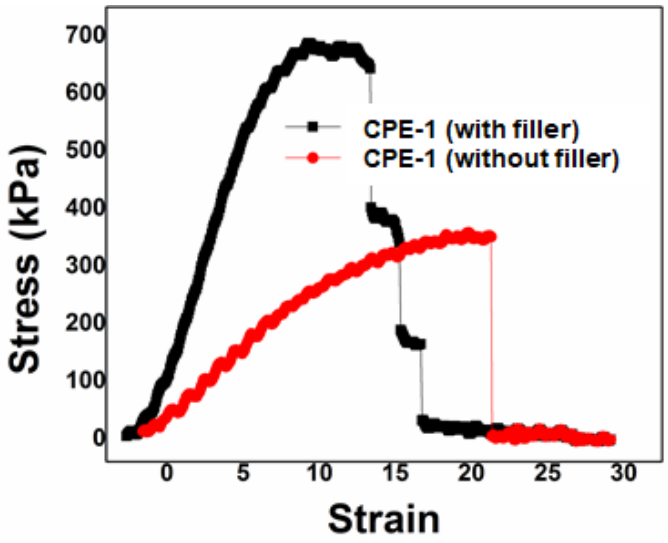


Areal capacities of high loading a) PCN/ZSM – Sulfur and b) PCS/ZSM-S nanocomposite material with respect to Li/Li$^+$ system. Gravimetric energy density of high loading c) PCN/IFM – Sulfur and d) PCS/IFM-S nanocomposite material

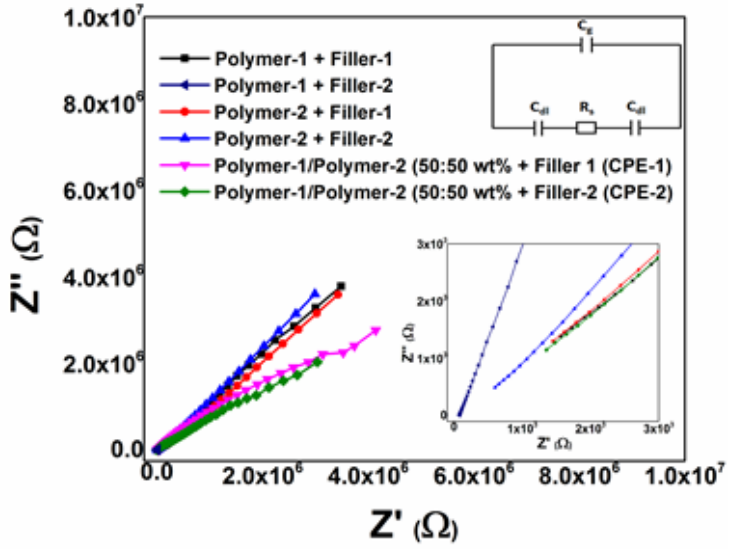
- **Active Material (AM):** Polymer with carbon and nitrogen (PCN)/IFM-S & Polymer Containing Sulfur (PCS)/IFM-S
- **Loading Electrode :** ~8-12mg/cm^2
  Slurry ~ 3 – 7mg/cm^2
  Loading AM : ~2.4–5.5 mg/cm^2
- **Slurry composition:** (PCN/IFM-S or PCS/IFM-S):Super P: PVDF (80:10:10)
- **(E) to sulfur (S) weight ratio:** 2:1 – 8:1 (2 - 8µl electrolyte:1mg AM)
- **Areal capacities:** ~4.25-4.75mAh/cm^2

Technical Back-Up Slides

Mechanical and Electrochemical properties of composite polymer electrolyte membrane used in the 3DP-LIC-CMC-S electrode architecture



Mechanical testing of CPE



Ionic conductivity measurement of CPE

GPE Composition	Ionic Conductivity (mS cm^{-1})
Polymer-1 + Filler-1	1.351
Polymer-1 + Filler-2	3.153
Polymer-2 + Filler-1	3.654
Polymer-2 + Filler-2	2.997
Polymer-1 + Polymer-2 (50:50 wt%) + Filler-1 (CPE-1)	2.091
Polymer-1 + Polymer-2 (50:50 wt%) + Filler-2 (CPE-2)	2.839
Liquid Electrolyte	4.283